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POLYMORPHISM OF COPPER SULFIDES IN THE SYSTEM $Cu_2S-Cu_{1.8}S$[1]

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ABSTRACT. Four mineral species have been determined in the system $Cu_2S-Cu_{1.8}S$. They are chalcosine Cu_2S, djurlite $Cu_{1.96}S$, a new hexagonal copper sulfide $Cu_{1.9}S$ (E. N. Yeliseyev [9]) and digenite $Cu_{1.8}S$. A precise diagnosis of the phases and their polymorphic modifications of copper sulfides may serve as an important criterion of physical-chemical conditions of the crystallization of native minerals in ores and chemical combinations in products of metallurgical alteration of copper sulfide and copper-nickel ores. The native copper sulfides of one or another composition originate as a result of oxidizing conditions in mineral formations. The data on copper sulfides, both minerals and artificial compounds in the system $Cu_2S-Cu_{1.96}S$ quoted in the paper may be considered standard.

The problem of the existence of polymorphic modifications in chalcocite Cu_2S is extremely important for refining diagnostics of minerals in pyritic deposits and for determining the phase composition in the products of metallurgical reduction of copper sulfides (pyritic and sulfide copper-nickel ores). The literature on copper pyrometallurgy [1, 12, 13 etc.] mentions only the presence of copper sulfide Cu_2S. The mineralogical literature contains much more information and many more opinions on the nature of chalcocite and related copper sulfides such as digenite $Cu_{1.8}S(Cu_9S_5)$. Contradictory data on the polymorphic modifications of copper sulfides have been the cause of the present situation of no reliable powder pattern data which could be used for diagnosing natural or artificial copper sulfides in the $Cu_2S-Cu_{1.8}S$ system. The study /385[2]

of polymorphism in copper sulfides is not only of practical importance for diagnosing minerals and artificial compounds, but may serve as a more reliable basis for rational classification of copper sulfides.

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[1] L.Ye. Rudenko, L.A. Sinev, B.L. Koshurnikov and N.I. Solovov participated in the experimental part of the work; L.Ye. Rudenko and L.A. Sinev -- in synthesis of the copper sulfides; N.I. Solovov and B.L. Koshurnikov -- in synthesis of copper-nickel converter mattes. X-ray analysis of the copper sulfides was undertaken by E.N. Yeliseyev and L.Ye. Rudenko, that of the converter mattes was undertaken by E.N. Yeliseyev and N.I. Solovov. The entire remainder of the work was done by E.N. Yeliseyev.

[2] Numbers in the margin indicate pagination in the foreign text.

Works on synthesis of copper sulfides are of great assistance in establishing the singularities of polymorphism in these compounds. An investigation of the conditions for phase stability in the $Cu_2S-Cu_{1.8}S$ system provides a basis for a better explanation of the conditions of mineral formation in nature, the existence of individual phases in the products of metallurgical reduction of copper sulfides, and also for refining the systematics of copper minerals (sulfides).

In this article an attempt is made to establish the entire range and effective boundaries of existence of copper sulfide modifications in the $Cu_2S-Cu_{1.8}S$ system on the basis of the available materials in the literature and the results of synthesis of copper sulfides under various conditions, as well as data on crystallization of copper sulfides from converter mattes of the copper-nickel metallurgical industry.

Natural Modifications of Copper Sulfides in the $Cu_2S-Cu_{1.8}S$ System

Ye. K. Lazarenko [10] considers the problem of the existence of polymorphic modifications -- "varieties" -- of chalcocite under natural conditions in the pyritic deposits of the Central Urals. His opinion is that there are several varieties of chalcocite in the pyrite beds: (1) most abundant is a bluish-white, strongly anisotropic copper sulfide; (2) comparatively rare is a laminar form, strongly anisotropic and found in small grains (the laminar nature shows up most clearly with etching, which reveals small plates of grayish-blue copper sulfide in blue chalcocite); (3) a dark blue isotropic copper sulfide which forms thin borders around the bluish-white form or fine veins in bornite; (4) a pinkish-white copper sulfide which is weakly anisotropic, develops together with the bluish-white form, and is extremely difficult to separate from this form. Lazarenko assumes that "these varieties are individual mineral forms of the chalcocite group, which has not yet been studied nearly enough" [10, page 144]. He gives a brief history of the studies on minerals in the chalcocite group and of the views relating to the existence in nature of not only a rhombic, but a cubic modification of chalcocite [10, pages 144-146]. It is pointed out in this connection that it was only the impact of N. Buerger's experiments [14] which brought about the recognition of the existence of copper sulfide with cubic symmetry in the crystal lattice. P. Ramdohr [19] proposed the name *neodigenite* for this modification in 1943.

The nature of cubic chalcocite -- neodigenite, or as it is now called *digenite*, has been explained by N.V. Belov [2, 3]. According to Belov, a deficiency of cations (copper) is covered by conversion of part of the copper cations from the univalent to the bivalent state. The role of bivalent copper in the composition of copper sulfides is illustrated by the $Cu^{1+}-Cu^{2+}-S$ phase diagram (Fig. 1), and also by Tables 1 and 2.

C.P. Grigor'yev [7, 8] experimentally confirmed the existence of cubic copper sulfide (digenite) and pointed out the diagnostic characteristics of this mineral. Later A. G. Betekhtin [5] expressed doubt as to the
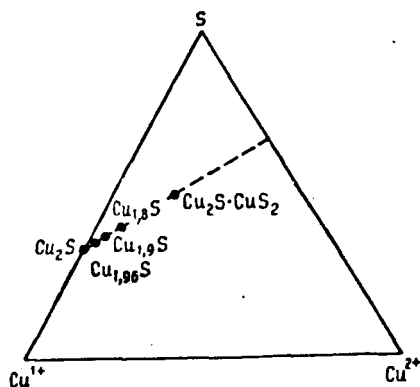
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Figure 1. Diagram of the Cu^{1+}-Cu^{2+}-S System (according to E.N. Yeliseyev): Cu_2S -- chalcocite; CuS or $Cu_2S \cdot CuS_2$ -- covellite; $Cu_{1.96}S$ -- djurleite; $Cu_{1.9}S$ -- new form of copper sulfide.

reliability of these characteristics, and rejected arguments in support of introducing the terms digenite and neodigenite into mineralogy.

Of the varieties of chalcocite mentioned by Ye. K. Lazarenko as found among the pyrites of the Central Urals, the dark blue isotropic form belongs to the digenite class. To confirm this conclusion, Ye. K. Lazarenko gives data on chemical analysis of a number of specimens for which computation from the analytical results yields the formula $Cu_{1.83}S$-$Cu_{1.84}S$ ([10, pp. 146-147], Tables 1 and 10). According to Lazarenko, digenite, as distinct from chalcocite, is found exclusively in the bornite ores of deep layers in the pyritic deposits of the Central Urals. In concluding his survey or mineralogical works on copper sulfides, he writes: "In view of the extremely inadequate study of minerals of the chalcocite group at the present time, perhaps both names should be retained in mineralogy, chalcocite being understood to mean the ordinary rhombic modification corresponding to the strict stoichiometric formula of Cu_2S, while digenite is understood to mean the cubic modification with formula $Cu_{2-x}S$, in which the copper deficiency is about 8% as compared with the first formula" [10, p. 145].

Experimental Research on Synthesis of Copper Sulfides

In 1915, E. Posnjak, E. Allen and H. Merwin[18] noted that the compound Cu_2S is polymorphic. According to the data given by these authors, rhombic chalcocite is converted to the cubic modification at 91°C. In conducting experiments on synthesis and high-temperature investigation of copper sulfides, N. Buerger noted [14] that rhombic chalcocite is converted to the hexagonal modification at 105°C. He established the existence of digenite, a compound with the composition $Cu_{1.8}S$ in the cubic crystal system. Later G. Donney, J. D. Donney and G. Kullerud [15] showed that digenite has a lower crystal lattice symmetry and should be classed with trigonal minerals. S. Djurle[1] [16] questioned the accuracy of the phase diagram for the

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[1] S. Djurle -- Swedish investigator of copper sulfides [see Ref. 16]. The correct pronunciation of this name is Yoorl, and the mineral named after him -- $Cu_{1.96}S$, djurleite -- is pronounced yoorlite. An initial "D" before the letter "j" in the Swedish language is silent. The combination of letters "Dju" is pronounced like English "you" (e.g., Ejup = Yoop). The final "e" in the name Djurle is not pronounced. In E.M. Bonshtedt-Kupletskaya's survey of new minerals (ZVMO, 1963, No. 5), djurleite is incorrectly transliterated as dzharleit.

TABLE 1.   ELEMENTARY CELL PARAMETERS FOR COPPER SULFIDES (IN kX)

Mineral type	Modification	Crystal system	Temperature (in °C)	Elementary cell parameters a_0	b_0	c_0
Chalcocite Cu_1S	I	Cubic	500	$5,735 \pm 0,010$	—	—
			465	$5,725 \pm 0,010$	—	—
	II	Hexagonal	460	$4,005$	—	$6,806$
			300	$3,981 \pm 0,004$	—	$6,761$
			152	$3,961$	—	$6,722$
	III	Rhombic	20	$11,881 \pm 0,004$	$27,323 \pm 0,008$	$13,491 \pm 0,004$
Djurleite $Cu_{1.96}S$	I	Cubic	500	$5,707 \pm 0,006$	—	—
	II	Tetragonal	20	$4,008 \pm 0,002$	—	$11,268 \pm 0,006$
	III	Low (?)	20	Powder pattern not deciphered		
New compound $Cu_{1.9}S$	—	Hexagonal	20	$11,332 \pm 0,007$	—	$13,479 \pm 0,015$
Artificial modification of digenite (from S. Djurle) $Cu_{1.8}S$	I	Cubic	500	$5,639$ $\pm 0,006$	—	—
			300	$5,610$	—	—
	II	Cubic	152	$5,593$ $\pm 0,006$	—	—
			80	$5,577$	—	—
	III	Cubic	20	$5,565$	—	—
Digenite $Cu_{1.8}S$	IV	Cubic (?) or trigonal (pseudocubic)	20	(depending on composition with a sulfur content of 35-37 at.%)		
			20	$a_{rh}=16,16$; $\alpha = 13°56'$ (trigonal cell) $a_0 = 27,71$ (5,54×5) (Pseudocubic cell)		

Note: The data for high-temperature modifications are taken from S. Djurle [16];   data   on   natural digenite are taken from G. Donney, J.D. Donney and G. Kullerud   [15].   The new hexagonal form was first mentioned in 1960 [9];   the   elementary cell parameters for this compound were determined by E.N. Yeliseyev (a_0 from reflections $22\overline{4}0$, $50\overline{5}0$, $51\overline{6}0$ and $43\overline{7}0$, and c_0 after computing a_0 from reflections $21\overline{3}7$, $11\overline{2}8$, $41\overline{5}8$ and $22\overline{4}9$).

Cu_2S-CuS system, published in 1941 by N. Buerger, and criticized Buerger for his method of sample preparation. (N. Bureger had pressed chalcocite and CuS powders and placed them in an open glass tube where they were heated to a temperature of the order of 110°C for at least 12 hours; this is an unsatisfactory method for treating the specimens, and Buerger himself came to the conclusion that chalcocite begins to change to digenite when heated in direct contact with air). Another result of S. Djurle's experiments was the establishment of a previously unknown variety of chalcocite -- $Cu_{1.96}S$. The greatest discrepancy between Djurle's results and those of previous investigators of the Cu_2S-CuS system lies in the discovery of an extensive region of homogeneity of highly symmetric modifications of copper sulfides at high temperatures.

TABLE 2. RESULTS OF CHEMICAL ANALYSIS OF "ARTIFICIAL" CONVERTER MATTES HARDENED AT VARIOUS TEMPERATURES

Specimens / Components	CuS Theoretical composition	$Cu_{1.8}S$ New data	$Cu_{1.92}S$ New data	Cu_2S -- Monchegorsk "artificial" samples of N.I. Solovov 100°C	200°C	600°C	700°C	800°C	Cu_3S Theoretical composition	$Cu_{1.96}S$ Theoretical composition
		2	3	4	5	6	7	8		
Cu	66,46	77,40	78,54	75,03	76,90	77,38	78,39	76,83	79,86	79,52
Ni	-	—	—	3,61	1,00	0,89	0,82	1,71	-	-
Fe	-	—	—	0,13	0,2	0,26	0,31	0,23	-	-
Co	-	—	—	0,63	0,57	0,60	0,06	0,68	-	-
S	33,54	21,59	20,61	20,25	20,34	20,03	20,39	19,51	20,14	20,48
Σ	100%	98,99%	99,15%	99,65%	99,01%	99,16%	99,97%	98,96%	100%	100%

Note: Crystallochemical formulas of the copper sulfides: specimen 1 -- covellite $Cu_2^{1+}S \cdot Cu^{2+}S_2$ or CuS; specimen 2 -- digenite (cubic chalcocite) $Cu_{1.6}^{1+}Cu_{0.2}^{2+}S$ or Cu_9S_5; specimen 3 -- new "hexagonal copper sulfide" $Cu_{1.84}^{1+}Cu_{0.08}^{2+}S$ or $Cu_{9.6}S_5$; specimen 9 -- chalcocite (rhombic copper sulfide) $Cu_{2.0}^{1+}S$ or $Cu_{10}S_5$; specimen 10 -- djurleite ("tetragonal chalcocite") $Cu_{1.92}^{1+}Cu_{0.04}^{2+}S$ or $Cu_{9.8}S_5$. Chemical analysis of the converter mattes was done at the chemical laboratory in the plant lab shop of the "Severonikel'". Combine under the direction of S. Ye. Kreymer.

The region of homogeneity for $Cu_{1.8}S$ is now represented entirely differently. N. Buerger's phase diagram [14] (Fig. 2) shows the existence of digenite with the ideal formula Cu_9S_5 ($Cu_{1.8}S$) below 78°C, whereas considerable solubility of Cu_2S or CuS in digenite is observed below this temperature. These phase ratios in the Cu_2S-CuS phase system exist only in cases where the system is open to admit oxygen. The composition of the initial material can change only during contact with air. This effect is not observed when either chalcocite Cu_2S or digenite $Cu_{1.8}S$ is heated in sealed tubes.

S. Djurle showed that the composition of the copper sulfides remains constant, and that only their crystal structure is disrupted. Djurle established the presence of three polymorphic states for each of the copper sulfides in the Cu_2S-$Cu_{1.8}S$ system, viz (Table 1): Cu_2S-I -- face-centered cubic cell; Cu_2S-II -- hexagonal chalcocite; Cu_2S-III -- rhombic chalcocite; $Cu_{1.96}S$-I -- new cubic compound; $Cu_{1.96}S$-II -- tetragonal compound at room temperature; $Cu_{1.96}S$-III -- compound of low symmetry (crystal system not established). All three modifications of $Cu_{1.8}S$ (I, II and III) differ from one another only in the dimensions of the cell (all three belong to the cubic crystal system).
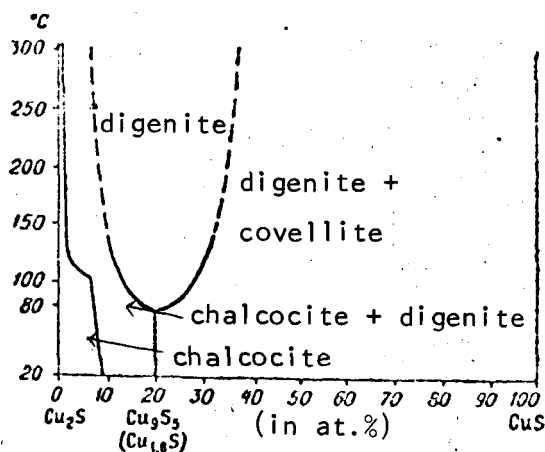
Figure 2. Phase Diagram of the Cu_2S-Cus System (according to Buerger, [14]).

S. Djurle [16] gave data on the elementary cell parameters of most of the polymorphic modifications of the three varieties of "chalcocite" which he mentions (see Table 1). Djurle's results give a clear definition of the boundaries of homogeneity for the cubic phases of copper sulfides, and finally settle the issue of the "chalcocite" and "digenite" problems which had been of concern to mineralogists until comparatively recently. Digenite and its polymorphic modifications are $Cu_{1.8}S$-I, $Cu_{1.8}S$-II and $Cu_{1.8}S$-III. "Cubic chalcocite" is actually not digenite, but rather a natural or synthetic chalcocite which has been converted to a high-temperature polymorphic modification -- Cu_2S-I (i.e., chalcocite heated in sealed evacuated tubes to temperatures exceeding 465°C). At temperatures of 152-460°C, Djurle established the existence of a moderate-temperature polymorphic modification of

chalcocite (Cu_2S-II) -- a hexagonal modification which is converted upon cooling to the rhombic Cu_2S-III. Shown in Figure 3 are S. Djurle's data for the variation in the elementary cell parameter of cubic modifications of various copper sulfides. These data were obtained under closed conditions /390 (with respect to atmospheric oxygen). There are obvious differences between the phase diagrams of the Cu_2S-$Cu_{1.8}S$ system under open conditions (see Figure 2) and under closed physicochemical conditions (see Figure 3).

The results of S. Djurle's x-ray analysis of copper sulfides [16] settle once and for all the doubts concerning the advisability of introducing into mineralogy not only the term "digenite", but also a new name for the compound $Cu_{1.96}S$, which is intermediate between chalcocite and digenite. E.H. Roseboom, with the agreement of N. Morimoto, who discovered the mineral with this composition in nature at the same time (see the reference to N. Morimoto's work in Reference [20] by E.H. Roseboom), called the natural modification of $Cu_{1.96}S$-III "djurleite".

In studying the phase composition of cooled copper-nickel converter mattes, E. N. Yeliseyev [9] discovered another phase intermediate between chalcocite and digenite, namely $Cu_{1.9}S$ with hexagonal crystal lattice symmetry. Data are given in Tables 1, 2 and 3 on the chemical composition, elementary cell parameters and powder pattern parameters of the new hexagonal copper sulfide phase in the Cu_2S-$Cu_{1.8}S$ system.

Synthesis of Copper Sulfides

In 1961, in the copper pyrometallurgy laboratory of the experimental research shop at the Noril'sk Mining and Metallurgy Combine, E. N. Yeliseyev and L. Ye. Rudenko, under the direction of L. A. Sinev, produced melts of pure copper sulfide in an air atmosphere. The copper sulfide was slowly roasted beneath a layer of activated charcoal to reduce the copper, which was partially oxidized to the bivalent state during melting in atmospheric oxygen. After protracted annealing beneath the activated charcoal layer, the copper sulfide was cooled and hardened.

The initial copper sulfide was produced by direct fusion of electrolytic copper and sticks of elemental sulfur; the stick sulfur was immersed in the molten copper with an excess of sulfur over the theoretical ratio for the formula of copper sulfide Cu_2S, since nearly 70% of the sulfur was burned up during the melting process. Melting was continued until the elemental sulfur had burned out, i.e., until the greenish flame (burning sulfur) above the crucible disappeared and the odor of burnt sulfur had subsided. The crucible containing the copper sulfide was then cooled and hardened beneath a jet of cold water.

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TABLE 3. DATA OF COPPER SULFIDE POWDER PATTERNS

Covellite CuS			Artificial digenite Cu$_{1.8}$S			New copper sulfide Cu$_{1.92}$S			Chalcocite subjected to protracted annealing and quenching at various temperatures									
1			2			3			4		5		6		7		8	
hkil	I	dα/n	hkl	I	dα/n	hkil	I	dα/n	I	dα/n	I	dα/n	I	dα/n	I	dα/n	I	dα/n
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1	4,048	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	111β	1	3,570	—	—	—	—	—	—	—	—	—	—	—	—	—
10ī0	4	3,33	—	—	—	—	—	—	—	—	1	3,333	—	—	—	—	—	—
10ī1	6	3,24	111	2	3,286	30̄30 / 21̄3̄2	2	3,255	—	—	2	3,273	—	—	—	—	—	—
—	—	—	—	—	—	30̄31	1	3,149	—	—	—	—	—	—	—	—	1	3,105
10ī2	8	3,04	200β	1	3,058	—	2	3,032	—	—	2	3,029	1	3,024	—	—	—	—
—	—	—	—	—	—	—	—	—	1	3,016	—	—	—	—	1	3,013	2	3,000
—	—	—	—	—	—	11̄24 / 30̄3̄2	1	2,916	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	22̄40	3	2,832	2	2,818	2	2,816	—	—	2	2,818	—	—
10ī3	10	2,81	—	—	—	202̄4 / 22̄4̄1	10	2,811	—	—	—	—	—	—	—	—	2	2,805
0006	8	2,72	200	4	2,750	—	—	—	5	2,721	7	2,738	3	2,742	8	2,731	5	2,725
—	—	—	—	—	—	30̄3̄3	2	2,639	1	2,633	1	2,668	—	—	—	—	—	—
—	—	—	—	—	—	31̄4̄2	4	2,535	2	2,538	2	2,547	—	—	2	2,548	1	2,535
—	—	—	—	—	—	40̄4̄0	1	2,468	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	22̄4̄3	4	2,396	2	2,331	5	2,396	2	2,393	3	2,388	1	2,384
10ī5	6	2,30	—	—	—	40̄4̄2	10	2,303	—	—	7	2,305	—	—	8	2,302	—	—
—	—	—	—	—	—	—	—	—	5	2,300	—	—	4	2,298	—	—	6	2,290
—	—	—	—	—	—	0006 / 32̄5̄0	2	2,261	1	2,250	1	2,261	—	—	1	2,256	1	2,254
—	—	—	—	—	—	10ī6	2	2,210	1	2,202	2	2,203	—	—	—	—	—	—
—	—	—	—	—	—	22̄4̄4	2	2,174	1	2,156	2	2,161	1	2,199	1	2,196	1	2,190
—	—	—	—	—	—	30̄3̄5	10	2,073	2	2,056	2	2,063	—	—	1	2,070	1	2,083
10ī6	4	2,03	—	—	—	40̄4̄4	10	2,000	—	—	—	—	—	—	10	2,000	8	2,004
—	—	—	—	—	—	—	—	—	7	1,993	10	1,998	6	1,984	—	—	—	—
—	—	—	220	10	1,965	50̄5̄0 / 22̄4̄5	10	1,964	—	—	10	1,963	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	7	1,953	—	—	—	—	10	1,955	8	1,960

TABLE 3.
(Continued)

Natural chalcocite Cu$_2$S			Natural djurleite Cu$_{1.94}$S		Artificial djurleite		Djurleite		Chalcocite			Digenite			
9			10		11		12		13			14			
hkl	I	da/n	I	da/n	I	dx/n	I	da/n	hkl	I	da/n	hkl	h'k'l'	I	dx/n
—	—	—	1	4,28	weak	4,291	10	4,30	---	—	—	—	—	—	—
—	—	—	1	3,89	"	3,893	16	3,89	300	0,5	3,93	—	—	—	—
133; 320; 062	2	3,74	2	3,752	mod.	3,751	13	3,75	133; 320; 062	1	3,77	—	—	—	—
260	2	3,58	2	3,586	weak	3,593	10	3,60	260	1	3,58	—	—	—	—
—	—	—	5	3,386	mod.	3,381	33	3,38	340; 060	3	3,39	—	—	—	—
—	—	—	1	3,35	—	—	—	—	233; 153	1	3,31	—	—	—	—
180	4	3,29	3	3,282	weak	3,278	7	3,27	—	—	—	—	—	—	—
—	4	3,17	3	3,192	"	3,191	16	3,19	180	2	3,25	111	555	4	3,21
—	—	—	2	3,100	"	3,102	10	3,09	—	—	—	—	—	—	—
342; 082	4	3,07	3	3,04	"	3,038	18	3,03	342; 082	2	3,05	—	199	1	3,05
—	—	—	3	3,01	"	3,014	20	3,01	—	—	—	—	—	—	—
400	4	2,95	—	—	"	2,965	—	—	400	0,5	2,97	—	—	—	—
					"	2,940									
—	—	—	—	—	"	2,892	7	2,89	420	2	2,88	—	—	—	—
—	—	—	(2	2,89	"	2,885	(7	2,88	—	—	—	—	—	—	—
—	—	—	(2	2,87	"	2,867	(10	2,87	—	—	—	—	—	—	—
420	4	2,84	1	2,82	"	2,833	(15	2,82	191	0,5	2,84	—	—	—	—
					"	2,816	(13	2,81							
—	—	—	0,5	2,78	"	2,788	7	2,78	---	—	—	002	0.0.10	4	2,74
362; 440; 420	5	2,73	1	2,69	"	2,691	9	2,74	362; 440; 402	1	2,73	—	—	—	—
282	2	2,64	1	2,654	"	2,655	5	2,66	282	1	2,67	—	—	—	—
—	—	—	0,5	2,595	"	2,601	13	2,59	380	0,5	2,58	—	—	—	—
304	4	2,55	1	2,557	"	2,561	13	2,56	304	1	2,54	—	1.1.11	0,5	2,53
—	—	—	0,5	2,514	"	2,519	9	2,51	—	—	—	—	—	—	—
460	4	2,48	1	2,477	"	2,477	7	2,47	460	2	2,47	—	—	—	—
382; 344; 084	7	2,40	0,5	2,41	"	2,417	5	2,41	382; 344; 084	7	2,40	—	4.4.10	0,5	2,40
—	—	—	9	2,387	str	2,391	82	2,39	—	—	—	—	—	—	—
520; 274	4	2,33	—	—	weak	2,318	(20	2,36	520; 274	0,5	2,34	—	—	—	—
							(7	2,32							
—	—	—	0,5	2,289	"	2,292	7	2,27	—	—	—	—	—	—	—
006	4	2,23	—	—	—	—	10	2,20	006	2	2,22	—	—	—	—
—	—	—	—	—	—	—	15	2,18	—	—	—	—	199	1	2,17
—	—	—	0,5	2,142	weak	2,144	5	2,14	0.12.2	1	2,14	—	—	—	—
275	2	2,11	0,5	2,107	"	2,109	7	2,11	—	—	—	—	—	—	—
—	—	—	1	2,069	"	2,071	7	2,07	—	—	—	—	—	—	—
—	—	—	0,5	2,047	"	2,048	9	2,05	275	1	2,06	—	—	—	—
600	10	1,99	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	9	1,964	mod.	1,965	100	1,96	600	8	1,969	022	0.10.10	10	1,97
—	—	—	9	1,957	mod.	1,958	(18	1,94	580; 504	0,5	1,937	—	—	—	—
							(9	1,92							

TABLE 3.
(Continued)

1			2			3			4		5		6		7		8	
hkil	I	da/n	hkl	I	da/n	hkil	I	da/n	I	d/an	I	da/n	I	da/n	I	da/n	I	da/n
0008	10	1,890	—	—	—	(3360/5052)	9	1,881	7	1,866	10	1,873	5	1,878	9	1,873	6	1,883
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	(3118/300?)	1	1,873	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	5160	3	1,762	1	1,761	2	1,762	2	1,765	2	1,765	4	1,762
(1120/1017)	8	1,730	—	—	—	(5162/2137)	8	1,707	—	—	—	—	—	—	—	—	7	1,707
—	—	—	—	—	—	—	—	—	3	1,697	8	1,699	2	1,699	9	1,697	—	—
—	—	—	311	2	1,675	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	(1128/4370)	4	1,614	1	1,616	1	1,614	—	—	2	1,617	2	1,618
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
(1018/1124)	3	1,555	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1126	4	1,465	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1	1,497
—	—	—	400	5	1,410	—	—	—	3	1,401	—	—	—	—	—	—	7	1,405
(2025/1·0·1·10)	4	1,382	—	—	—	—	—	—	1	1,359	3	1,399	1	1,399	5	1,399	—	—
1128	6	1,347	—	—	—	6066	5	1,325	3	1,321	2	1,322	1	1,322	4	1,325	5	1,326
2027	6	1,272	—	—	—	7182	4ш	1,270	1	1,257	1	1,255	—	—	2	1,260	2	1,265
2028	6	1,210	—	—	—	(6067/7075)	5ш	1,243	1	1,229	1	1,230	—	—	2	1,234	—	—
—	—	—	422	1	1,134	—	—	—	2	1,196	1	1,194	—	—	2	1,195	—	—
2133	8	1,093	511	1	1,084	—	—	—	—	—	—	—	—	—	2	1,087	—	—
3032	6	1,056	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
3034	6	1,014	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0·0·0·16	4	0,990	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Note: Columns 1-11 give the results of x-ray analysis of the various copper sulfides for which the results of chemical analysis are given in Table 2. The specimens are: 1--covellite according to V.I. Mikheyev [11]; 2--artificial digenite (new data); 3--new hexagonal copper sulfide (unnamed); 4-8--sulfide melt which in the initial state had the same ratio of copper to sulfur as in chalcocite and was quenched after protracted annealing at various temperatures: 8--at 800°C, 7--at 700°C, 6--at 600°C, 5--at 200°C and 4--at 100°C (all specimens were cooled simultaneously with successive quenching of the copper sulfides as the temperatures indicated above were reached; the last specimen, which was cooled to 100°C, was taken out of the furnace after five
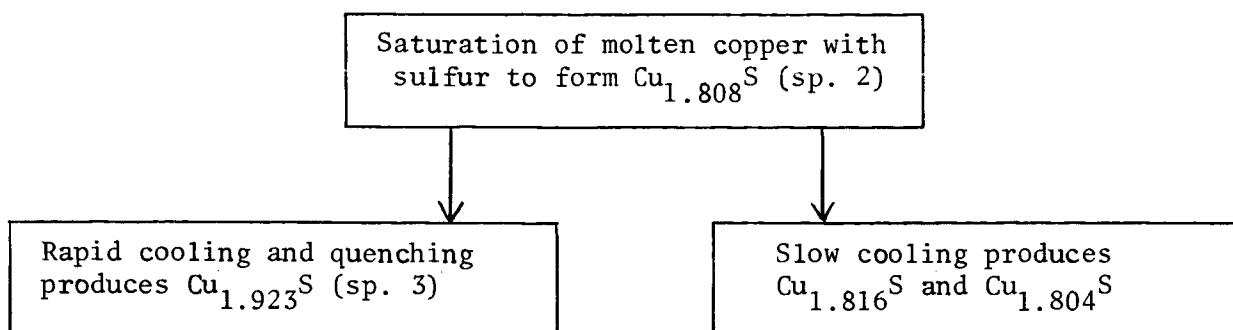
TABLE 3.
(Continued)

9			10		11		12		13			14			
hkl	I	da/n	I	da/n	I	da/n	I	da/n	hkl	I	da/n	hkl	h'k'l'	I	da/n
0·12·4; 3·12·2 346; 086	10	1,89	10	1,871	str.	1,871	96	1,87	0·12·4; 3·12·2 346; 086	10	1,870	—	—	0,5	1,877
—	2	1,85	—	—	weak	1,832	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	366; 395; 406	0,5	1,787	—	999	0,5	1,781
—	5	1,72	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	2	1,693	mod.	1,691	—	—	604; 0·16·0	4	1,695	—	—	—	—
—	—	—	1	1,683	weak	1,681	—	—	(682;644 0·16·2	2	1,645	113	5·5·15	3	1,686
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0·12·6	2	1,593	—	—	—	—	—	—	0·12·6	0,5	1,588	—	—	—	—
—	2	1,545	—	—	weak	1,514	—	—	684; (3·16·2 0·16·4	2	1,514	—	—	—	—
3·12·6	2	1,484	—	—	—	—	—	—	3·12·6	0,5	1,471	—	—	—	—
—	2	1,414	—	—	—	—	—	—	—	—	—	—	—	—	—
—	2	1,371	—	—	—	—	—	—	—	—	—	004	0·0·20	1	1,395
—	2	1,338	—	—	—	—	—	—	686; (0·16·6 0·12·3	1	1,351	—	1·2·21	0,5	1,320
—	4ш	1,293	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	mod.	1,274	—	—	(3·20·0; 608 3·16·6	3	1,278	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	2ш	1,133	—	—	weak	1,121	—	—	(9·12·2; 946 0·0·12; 0·24·2	1	1,119	224	10·10·20	2	1,139
—	4	1,091	—	—	—	—	—	—	(9·12·4; 986 0·24·4	1	1,074	(115 333	5·5·25 15·15·15	1	1,074
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	(3·24·6; 12·4·0 3·12·12	1	0,974	044	0·20·20	1	0,986
—	—	—	—	—	—	—	—	—	—	—	—	135	5·15·25	1	0,943

days); 9--natural chalcocite according to V.I. Mikheyev [11]; 10--natural djurleite according to E.A. Roseboom [20]; 11--artificial compound Cu$_{1.96}$S-III, synthesized for the first time by S. Djurle [16]; 12--natural djurleite according to N. Morimoto [20]; 13--chalcocite from Mexico according to L.G. Beirry and R.M. Thompson [21] [sic]; 14--digenite from the Leonard Mine in Butte, Montana according to N.W. Buerger [14]. The hkl indices are given for digenite for the cubic cell computed by W. Kurz [17], and also the h'k'l' indices for the rhombohedral cell according to G. Donney, J. D. Donney and G. Kullerud [15].

Data on the chemical composition of copper sulfides are given in Table 2, and the results of x-ray analysis of various copper sulfides are given in Table 3. The data given in Table 3 may be used as standard data for decipering the mineral composition of sulfide ores, and also the phase composition of products of metallurgical reduction of copper and copper-nickel sulfide ores.

Data are given in Table 2 on the empirical concentration of copper in the various mineral types of the $Cu_2S-Cu_{1.8}S$ sytem. A distinctive feature of copper sulfides is the defective nature of the crystal structures of these minerals. Vacancies appear at the copper lattice sites in the structure of these minerals under the effect of partial copper oxidation (under the effect of conversion of some of the copper cations from the univalent to the bivalent state). The crystallochemical formulas of copper sulfides of various composition take account of the presence of bivalent copper in these minerals (see note to Table 2).

Copper sulfide $Cu_{1.8}S$ produced by direct fusion of copper and sulfur (Table 3, specimen 2) was divided into three parts, pulverized and remelted in three crucibles in an electric furnace for two hours at 1100°C under a layer of activated charcoal (to prevent oxidation of the copper). Then one of the crucibles was quickly cooled (quenched) under a jet of water while the two others were cooled over a period of 15 hours. Part of the slowly cooled specimen was broken up and remelted again at 1100°C (in this case the compound $Cu_{1.94}S$ was produced with tetragonal crystal lattice symmetry), and was then slowly annealed over a period of two days at 900°C under a layer of activated charcoal (here hexagonal copper sulfide $Cu_{1.914}S$ was produced). Thus copper sulfides were synthesized according to the following shceme:

```
                    ┌─────────────────────────────────┐
                    │ Saturation of molten copper with│
                    │ sulfur to form Cu₁.₈₀₈S (sp. 2) │
                    └─────────────────────────────────┘
                         │                    │
                         ▼                    ▼
┌──────────────────────────────┐  ┌──────────────────────────────┐
│ Rapid cooling and quenching  │  │ Slow cooling produces        │
│ produces Cu₁.₉₂₃S (sp. 3)    │  │ Cu₁.₈₁₆S and Cu₁.₈₀₄S        │
└──────────────────────────────┘  └──────────────────────────────┘
```

Saturation of molten copper with sulfur to form $Cu_{1.808}S$ (sp. 2)

Rapid cooling and quenching produces $Cu_{1.923}S$ (sp. 3)

Slow cooling produces $Cu_{1.816}S$ and $Cu_{1.804}S$

Note: The numbers of the specimens are the same as in Tables 2 and 3.

Copper Sulfides in Copper-Nickel Converter Mattes

In 1957-1958, E. N. Yeliseyev and N. I. Solovov used r-meter analysis for studying the phase composition of "artificial" converter mattes. It was found during this research that if the sulfide melts are not kept airtight during slow cooling, there is an increase in the ingrowths of other phases in addition to Cu_2S -- $Cu_{1.9}S$ and $Cu_{1.8}S$. Thus even when extremely limited quantities of atmospheric oxygen are present, the amount that can seep through the fireclay linear, nonequilibrium conditions are brought about for the existence of chalcocite (cu_2S), and as a result this mineral is converted first to hexagonal copper sulfide -- $Cu_{1.9}S$, and then to digenite -- $Cu_{1.8}S$ (Fig. 4). According to new data, chalcocite is first converted during "oxidation" (i.e., during transition of part of the copper from the univalent to the bivalent state, which indicates copper oxidation) to tetragonal copper sulfide $Cu_{1.96}S$--djurleite, and then to $Cu_{1.9}S$ and later to $Cu_{1.8}S$. Thus under oxidative conditions the valency state of the copper changes, resulting in the appearance of deficient compounds with an irrational ratio of copper to sulfur.

Specimens 4-8 (see Tables 2 and 3) were prepared as follows. Five identical parts of initial copper sulfide, after crystallization of the solid phases, were slowly cooled to temperatures of 800 (sp. 8), 700 (sp. 7), 600 (sp. 6), 200 (sp. 5) and 100°C (sp. 4), and quenched at this temperature. The results of chemical analysis of the "artificial" converter mattes (specimens 4-8) quenched at various temperatures are shown in Table 2, and the x-ray characteristics of these same samples are given in Table 3. For comparison, Tables 2 and 3 also contain data for Covellite, digenite and a new copper sulfide $Cu_{1.9}S$, as well as for chalcocite and djurleite. Given in Table 4 are data on the elementary cell parameters for the cubic modification of copper sulfide synthesized at various temperatures from an initial specimen of composition Cu_2S. These data show that high-temperature "chalcocite" ($Cu_{1.8}S$) undergoes thermal expansion in the 200-300°C range with an average coefficient of linear expansion of 0.000053 kX/°C at the edge of the elementary cell.

Significance of Data on the Presence of Polymorphic Modifications in Explaining the Physicochemical Conditions of Mineral Formation

The presence of a low-temperature or high-temperature modification of copper sulfides in ores may be used as a basis for indirect determination of the conditions under which the ores were formed. For instance, a microscopic examination of the chalcocite-rich ore from Klinnecott (Alaska) revealed that grains of "cubic chalcocite" are surrounded by borders consisting of rhombic chalcocite. The presence of both phases has been confirmed by x-ray analysis of these specimens [11].
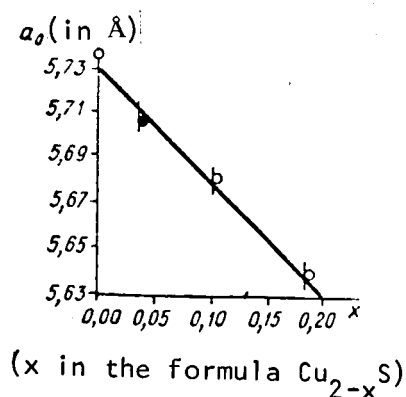
a_0(in Å)

5,73
5,71
5,69
5,67
5,65
5,63

0,00 0,05 0,10 0,15 0,20 x

(x in the formula $Cu_{2-x}S$)

Figure 3. Changes in the Parameter a_0 of Cubic Compounds $Cu_{2-x}S$ as a Function of the Deficiency of the Elementary Cell (x)(according to S. Djurle's data [16]).
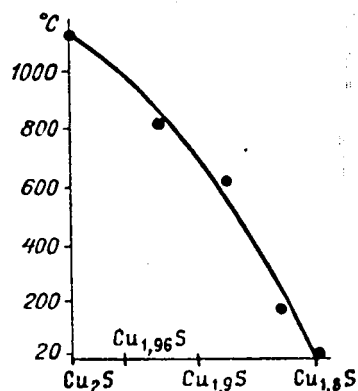
°C

1000
800
600
400
200
20

$Cu_{1,96}S$

Cu_2S $Cu_{1,9}S$ $Cu_{1,8}S$

Figure 4. Composition of Artificial Copper Sulfide as a Function of Quenching Temperature. Cooling from 1100°C to 200 and 20°C over a period of five days.

TABLE 4. DIMENSIONS OF THE ELEMENTARY CELL OF THE CUBIC SULFIDE $Cu_{1.8}S$ AS A FUNCTION OF TEMPERATURE

Temperature in °C	Author	Deposit	Parameter a_0 (in kX)
20	Betman and Laski [Ref.6]	Arizona	5,552±0,002
20	Kurz [Ref. 17]	?	5,575±0,007
170	G.B. Bokiy [Ref. 4]	?	5,564
After quenching at 200	E.N. Yeliseyev & N.I. Solovov (new data)	From alloys	5,588
After quenching at 600	•	•	5,596
After quenching at 700	•	•	5,595
After quenching at 800	•	•	5,620

Note: The "artificial" converter mattes used for determining the elementary cell dimensions of the cubic phase $Cu_{1.8}S$ were produced under the direction of B.L. Koshurnikov in the experimental research shop of the "Severonikel'" Combine.

Under experimental conditions, Cu_2S is a much more stable compound than, say, covellite CuS. During smelting of sulfide copper-nickel ores, artificial chalcocite is constantly present among the converter mattes. However, in spite of the considerable volume of research work which has been done by physical chemists and metallurgists, there are no data in the literature on the presence of any given modifications of copper sulfides in the products of metallurgical reduction of copper-nickel sulfide ores. For the first time, we have established the presence of all modifications of copper sulfides in artificially prepared converter mattes crystallized in loosely sealed small crucibles (150-100 cm^3). The presence of several modifications of copper sulfide (rhombic Cu_2S, tetragonal or pseudotetragonal $Cu_{1.96}S$, hexagonal $Cu_{1.9}S$ and cubic $Cu_{1.8}S$) indicates absence of equilibrium during solidification of the sulfides. A rapid change in temperature facilitates preservation of nonequilibrium modifications of copper sulfides. An important part in the disruption of equilibrium during cooling of copper sulfides is played by atmospheric oxygen which, in contacting the copper, facilitates conversion of the element to the bivalent state (sulfur also facilitates oxidation of copper in sulfides). The tremendous difficulties in attaining equilibrium during crystallization of copper sulfides are convincingly pointed up by observing a suspension close in composition to Cu_2S melted in a reducing atmosphere at 1200°C in small crucibles (sealed with a ceramic plug and coated with a thick layer of fireclay cement). Equilibrium was not achieved in the Cu_2S-$Cu_{1.8}S$ system under these experimental conditions with slow cooling over a period of five days.

Neither have equilibrium conditions been achieved during the formation of copper sulfides in nature. Borders of some copper sulfides around others (as in the Klinnecott ores in Alaska) are evidence of changes in the oxidation-reduction conditions during formation of copper sulfide ores. For instance the growth of chalcocite borders around digenite indicates an increase in reduction conditions (potential) before the copper sulfides are finally formed, with the result that all the copper was already in the univalent state when the copper sulfides had finally crystallized (whereas some of the copper ions must be in the bivalent state for the formation of digenite).

The correct diagnosis of polymorphic modifications and varieties of copper sulfides in natural formations, as well as in the products of metallurgical reduction of ores, as shown above, may be of valuable assistance in explaining the physicochemical conditions of crystallization of these minerals and chemical compounds.

Regions of Homogeneity of Individual Phases in the Cu_2S-$Cu_{1.8}S$ System

It has been established that this system contains four mineral types which are stable at ordinary (about 20°C) temperatures (see Table 1):

1. A solid solution which is stable between Cu_2S and $Cu_{1.98}S$ -- chalcocite.

2.	A solid solution which is stable between $Cu_{1.95}S$ and $Cu_{1.97}S$ -- djurleite.

3.	A solid solution of composition $Cu_{1.92}S-Cu_{1.9}S$ -- a new hexagonal copper sulfide first mentioned by E. N. Yeliseyev [9].

4.	Cubic or pseudocubic $Cu_{1.8}S$ -- digenite.

In closed physicochemical systems (in sealed tubes without access to air) each of the copper sulfides goes through polymorphic transformations during heating -- modifications with higher symmetry are stable at higher temperatures (Table 1).

Copper is partially oxidized during heating under open physicochemical conditions (some of the copper ions become bivalent in sulfides) even when there is only a slight influx of atmospheric oxygen. Under these conditions, the "copper:sulfur" ratio changes (Fig. 4) in the copper sulfide, although the sum of the valences of the cations and anions in these sulfides remains the same. The concentration of bivalent copper increases in proportion to the number of defects in the structure of copper sulfides ($Cu_{2-x}S$), so that the general formula for all copper sulfides is of the form: $Cu_{2-y}^{1+}Cu_{0.5y}^{2+}S$. Under oxidative conditions, chalcocite gives rise to more "sulfurous" copper sulfides (djurleite, hexagonal sulfide or digenite) depending on the oxidative potential of the medium in which the chalcocite is heated or slowly cooled. With the formation of more "sulfurous" sulfides from chalcocite, some of the copper is excess and precipitates in the form of a metallic phase as segregations in the sulfides. The simultaneous presence of several copper sulfides in ores or products of metallurgical conversion of ores is convincing proof of nonequilibrium conditions during formation.

The Part Played by the Redox Potential in Formation of a Given Copper Sulfide $Cu_{2-x}S$

Under oxidative conditions, the univalent copper in copper sulfides is converted to the bivalent state:

$$Cu^{1+}-e^{-} = Cu^{2+}.$$
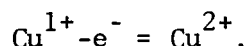
Experiments with heating of copper sulfides in sealed ampules away from atmospheric oxygen [16] show that the copper ratio for the different valence states remains constant, even at temperatures up to 500°C. During heating under these conditions, the low-temperature modifications of copper sulfides are converted to the high-temperature forms. Experiments with heating of these same copper sulfides in the presence of even small quantities of air show completely different results (see the experiments described above with slow cooling of sulfides in small crucibles sealed with a ceramic plug and coated with fireclay cement). The decomposition of digenite at temperatures above 78°C described by N. V. Buerger [14] was used as the basis

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for plotting the phase diagram of the Cu_2S-CuS system (Fig. 2). This decomposition is not observed in sealed tubes (Fig. 3). Hence it clearly follows that atmospheric oxygen is the principal agent responsible for oxidation of copper in reactions with copper sulfides during heating. The formation of djurleite from chalcocite during heating may be described as follows:

$$25 \cdot Cu_{2.0}^{+1}S - e^- = 25 \cdot Cu_{1.92}^{1+}Cu_{0.04}^{2+}S + Cu.$$
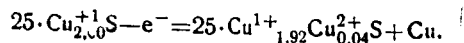
Djurleite and hexagonal copper sulfide ($Cu_{1.9}S$) may be encountered as an intermediate zone at contact between digenite and chalcocite.

On the Systematics of Copper Sulfides in the $Cu_2S-Cu_{1.8}S$ System

The crystal structure of all copper sulfides described above is based on extremely dense packing of sulfur anions which is distorted by structural defects (vacant copper sites) and by substitution of bivalent copper for the univalent form.

The comparatively easy transition from one mineral form of copper sulfides to another (see for instance Fig. 4) during heating under open physicochemical conditions is explained by the fact that the basic motifs of the crystal structure are maintained when the lattice symmetry in these copper sulfides changes (Cu_2S -- rhombic; $Cu_{1.96}S$ -- tetragonal; $Cu_{1.9}S$ -- hexagonal; $Cu_{1.8}S$ -- cubic crystal system).

During heating or formation of natural sulfides in open physicochemical systems, the quantitative ratio between copper and sulfur changes with a variation in the valence state of copper. However, with the converstion or transformation of one mineral form of copper sulfides to another, the crystal structure is inherited to a considerable extent as compared with the original copper sulfide. E. N. Yeliseyev [9] remarked that "the widespread prevalence of the phenomenon of inheritance of general features of the crystal structure in minerals of related composition should be given particular attention by distinguishing series of minerals with close chemical composition and similar structures -- series of minerals with inherited crystal structures" [9, p. 421].

The systematics of copper sulfides can have a truly crystallochemical basis only when consideration has been given to the inheritance of general characteristics of the crystal structure in all mineral forms of copper sulfides. All copper sulfides (chalcocite, djurleite, the new hexagonal copper sulfide, digenite and covellite) should be described together in the crystallochemistry of sulfides (and not separately as is done in the existing classifications of sulfides at the present time) under a single division, distinguishing a "series of minerals of copper sulfides with inherited crystal structures."

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